Title: Evaluation of Fly Ashes from the Henan Province of China for Use as Concrete Admixtures

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Summary:

China is undergoing rapid economic expansion, with attendant demands for energy and building materials. In particular, China's use of coal is expected to double in the next decade and concrete for buildings and highways will be in short supply. These demands for energy and materials could prove complementary if fly ash from the burning of coal can be used in concrete admixtures. The objective of this study is to evaluate the suitability of fly ashes from the Henan Province of China for use in concrete admixtures. A variety of analytical techniques to assess the carbon content of several fly ashes are compared in this study. The International Institute of Theoretical and Applied Physics is sponsoring this Sino-American collaboration at Iowa State University.

Thirteen fly ash samples from different coal-fired power plants in the province of Henan were collected by the Henan Center for Comprehensive Utilization of Fly Ash. The samples were shipped to the Center for Coal and the Environment (CfCE) at Iowa State University where each sample was divided into four aliquots and sealed in glass vials. Sets of aliquots assembled from the thirteen samples were labeled and distributed to the four groups providing analysis for the project: the Chinese Academy of Sciences, the Iowa State University (ISU) Department of Civil and Construction Engineering (CCE), Ametek Corporation, and the ISU CfCE. A variety of analytical techniques were employed by the groups to determine the unburned carbon content of the thirteen fly ash samples.

The Chinese Academy of Science used gravimetric methods to progressively determine moisture, inorganic carbon, and organic carbon. Samples were weighed, heated to 105 C for several hours, and then reweighed to determine moisture. Samples were then heated to 950 C in an inert nitrogen atmosphere for several hours before being cooled and reweighed to determine the amount of inorganic

carbon driven off, presumably as a result of carbonate decomposition. Finally, the remaining fraction was heated in oxygen to 750 C and the corresponding weight loss attributed to organic carbon. Adding the weight changes associated with heating in nitrogen and heating in oxygen gives the loss on ignition (LOI) value for the fly ash.

The ISU CCE Department directly performed the classical LOI test: after drying the samples they were heated in air to 750 C for a period of several hours after which the weight change was recorded as LOI. The CCE Department also provided a variety of chemical analyses to the samples, including X-ray diffraction (XRD) analysis and X-ray fluorescence (XRF) analysis to support other studies on the Chinese fly ashes.

Ametek used a carbon-in-ash analyzer recently licensed from Iowa State University to directly measure organic carbon. This instrument, the CA200 Carbon Analyzer, uses a modulated light-emitting diode (LED) to excite a thermal response in materials containing organic carbon. The thermal response subsequently generates a minute acoustical wave detectable by a microphone. This so-called photoacoustic effect produces a response that varies in proportion to the amount of carbon in fly ashes that have been prepared by grinding and compressing to a uniform pressure. Ametek also arranged for a commercial laboratory to analyze the fly ashes for organic carbon content. The steps of this analysis included treatment of the samples with acid to decompose carbonate minerals, drying and weighing of samples, firing the samples in an oxidizing environment, and recording the resulting weight change as organic carbon content.

The Center for Coal and the Environment tested samples with a new analytical technique based on the microwave-excited photoacoustic response. Microwave radiation at 1.0 GHz is absorbed by carbon in fly ash and generates an acoustical signal that is detected by a microphone. The expected advantage of this technique is that absorption of microwave radiation will be independent of the size of carbon particles, thus eliminating the need for preparing samples by grinding, as is done for the optically-based photoacoustic effect. However, the technique also responds to moisture and samples must be reasonably dry before tested for carbon.

The results of the various analyses are given in Table 1. The first observation is that several of the samples (Numbers 5,6,7,10, 12, and 13) had surprisingly high moisture content, exceeding 3% and ranging as high as 46.5%. Apparently, it is common in China to employ water sprays to scrub fly ash out of flue gas. Important changes in the chemical and physical properties of the fly ash can be expected under these circumstances and might account for some of the observations that follow despite the fact that all samples were thoroughly dried before analysis of carbon was undertaken.

The LOI determined by Chinese and American laboratories showed close agreement, which is expected from the similarity of the analytical methods employed for this measurement. The organic carbon determinations show large discrepancies at carbon concentrations less than about 2%, with the U.S. measurements running higher than the Chinese measurements. Such large discrepancies are common for low carbon fly ashes, even among replications from a single laboratory, as previous experience has indicated. However, at higher carbon concentrations the two measurements are in reasonable accord, despite differences in analytical techniques. Prior to firing samples to oxidize organic carbon, Chinese team members heated the samples in the absence of oxygen whereas American team members treated the samples with acid. Both actions would have the effect of decomposing carbonates in the samples, but presumably other mineralogical reactions could occur that add or subtract from the weight of the samples. The relatively good agreement between these two independent determinations of organic carbon suggests that either technique can be used with confidence to determine organic carbon content for concentrations above about 2%. However, an examination of the data demonstrates that LOI is a poor proxy for organic carbon in many instances.

The correlation between the optically-excited photoacoustic measurements made with the Ametek CA200 instrument and organic carbon content of the fly ashes is not as compelling as similar measurements made on U.S. fly ashes in previous studies. One possibility is that the process of water scrubbing employed in several of the power plants from which the Chinese fly ashes were obtained yielded a much wider range of thermal properties than is typical for American fly ashes. Indeed, the Chinese fly ashes showed considerable variation in fineness, as measured by the amount of ash that passed a 325 mesh sieve. Most American power plants remove fly ash with bag houses or electrostatic precipitators, which yield a dry fly ash product. Further investigation is required on this issue.

Results obtained with the microwave-based photoacoustic effect shows evidence of a linear response for carbon concentrations as high as 45%, in contrast to a characteristic “saturation” effect above about 10% for the optically-based photoacoustic effect. However, the scatter in the data is unacceptably high for use as an analytical instrument. Again, variations in the thermal properties of the fly ash as a result of hydration may be responsible for the poor correlation in signal. Although optical absorption of microwave radiation will be independent of particle size, the resulting thermal wave will depend on the size and physical properties of the fly ash.

Table 1. Results of analysis

	1	2	3	4	5	6	7	8	9	10	11	12	13
Moisture (%)	0.08	0.20	0.33	0.20	4.61	46.5	3.35	1.12	0.42	19.1	0.69	34.1	9.61
China LOI*	1.22	1.21	1.36	2.91	17.9	46.3	7.6	7.45	6.27	4.85	8.01	5.40	8.77
U.S. LOI*	1.09	1.28	1.41	2.76	16.2	48.3	6.64	6.73	6.04	5.13	7.79	4.38	8.84
China Org C*	0.42	0.13	0.14	1.03	12.1	41.8	2.44	4.56	4.40	2.21	6.08	1.29	5.61
U.S. Org C*	0.75	1.03	0.88	2.39	13.6	41.4	3.96	5.45	4.96	4.37	7.18	2.71	5.79
Optical PA**	100	99.3	92	136	162	192	132	134	144	132	133	131	134
MW PA**	13.8	12.0	11.3	7.0	26.1	119	24.2	15.7	12.0	18.2	19.0	18.3	23.1

*Weight-percent, dry basis (see text for description of analytical method employed)

**Optically-excited photoacoustic signal measured in millivolts

***Microwave (MW)-excited photoacoustic signal measured in microvolts